Effects of Mixing on Ammonia Oxidation in Combustion Environments at Intermediate Temperatures

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Outline

Flame Background

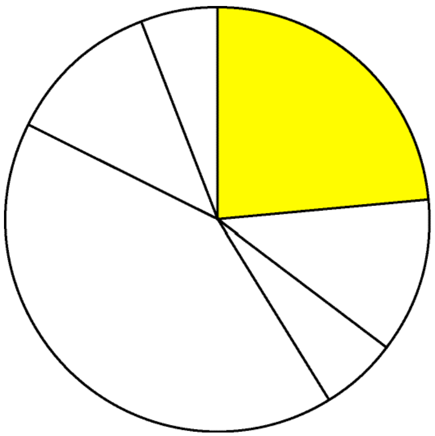
Experiment

Plug Flow Predictions

DNS Predictions

Zwieterung Predictions

Conclusions



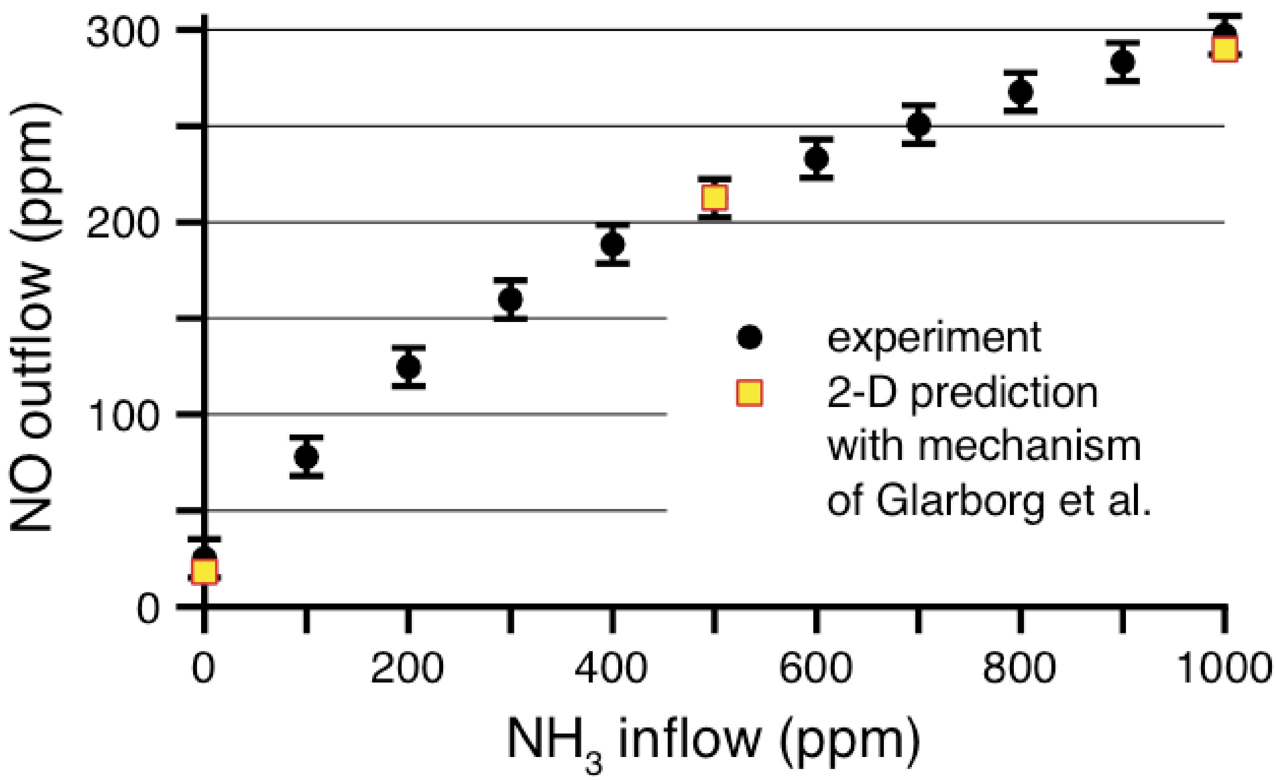
Ammonia in Flames

- Biomass releases nitrogen compounds as:
  - Ammonia
  - Hydrogen cyanide
- Fuel-bound nitrogen oxidizes to N_2 or NO
- NO selectivity varies with flame type:

Diffusion flames:	Selectivity declines with more Ammonia
Premixed flames:	Linear response

– Sarofim et al., *AIChE Symp. Series* (1975)
– Sullivan et al., *Combust. Flame* (2002)

Eg: Methane Diffusion Flame



<u>Fuel Ammonia</u>

1st 500 ppm NH_3

⇒

≈ 200 ppm NO

2nd 500 ppm NH_3

⇒

≈ 75 ppm NO

Flame:	Sullivan et al., *Combust. Flame* (2002)
Mechanism:	Glarborg et al., *Combust. Flame* (1998)
Fluid Dynamics:	Day and Bell, *Combust. Theory Modelling* (2000)

Selectivity in Diffusion Flames

$NH_3 \rightarrow NO$ selectivity depends on 2 effects:

1. Reactions between 2 nitrogen-bearing species,

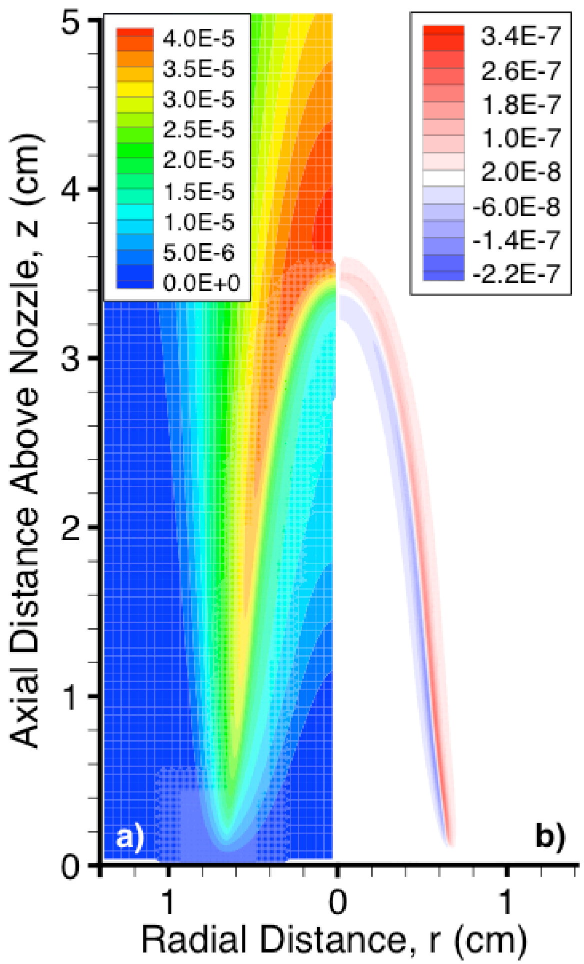
$$
\begin{aligned}
N + NO &\rightarrow N_2 + O \\
NH + NO &\rightarrow N_2O + H \\
&\rightarrow N_2 + OH \\
NH_2 + NO &\rightarrow N_2 + H_2O \\
&\rightarrow NNH + OH
\end{aligned}
$$

So more NH_3 lessens $NH_3 \rightarrow NO$ selectivity

2. Transport of NO to the rich side of the flame

Flame cycling of NO’s N atoms

X(NO) □(NO)

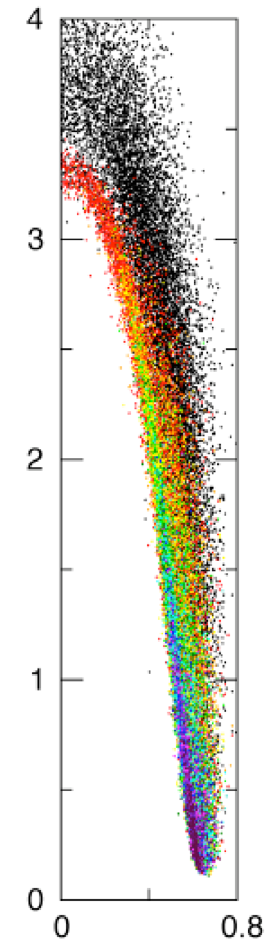


- (left) Two-step process:
  1. NO forms on the lean side
  2. Some NO diffuses to the rich side and forms either N_2 or HCN. The HCN then moves back to the lean side and forms either N_2 or NO …
  - Sullivan et al., *Combust. Flame* (2002)
- (right) Stochastic particles track N atoms that form NO
  - Black point: create only
  - Color point: first of 1 or more destruction cycles

    RED = 1 cycle

    PURPLE > 10 cycles
  - Bell, et al., *JCP* (to appear)

particle events



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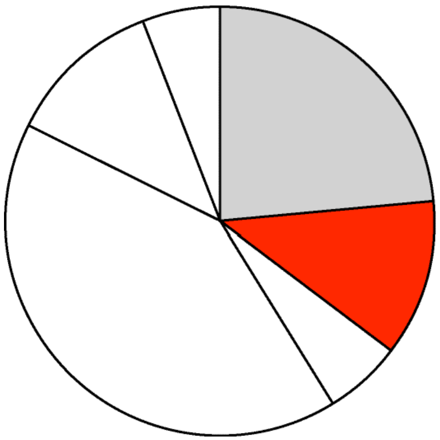
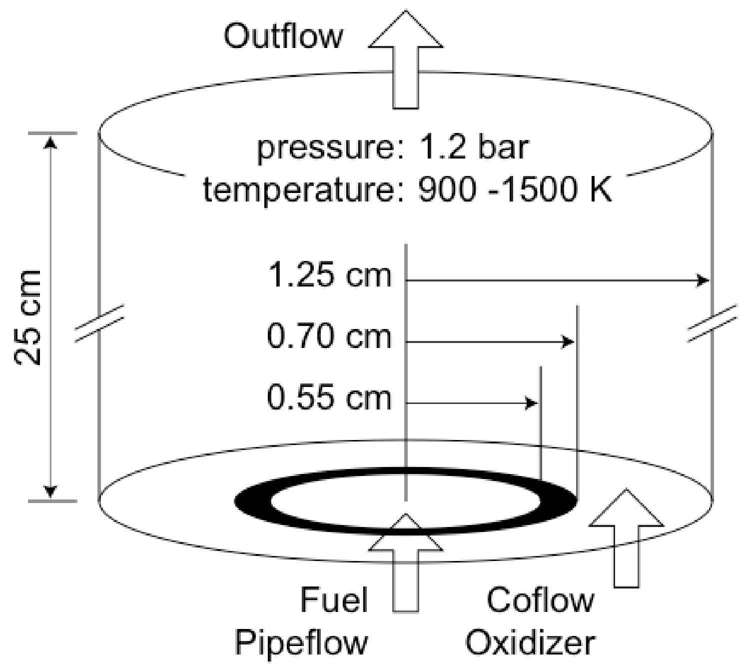


Isothermal Reactor



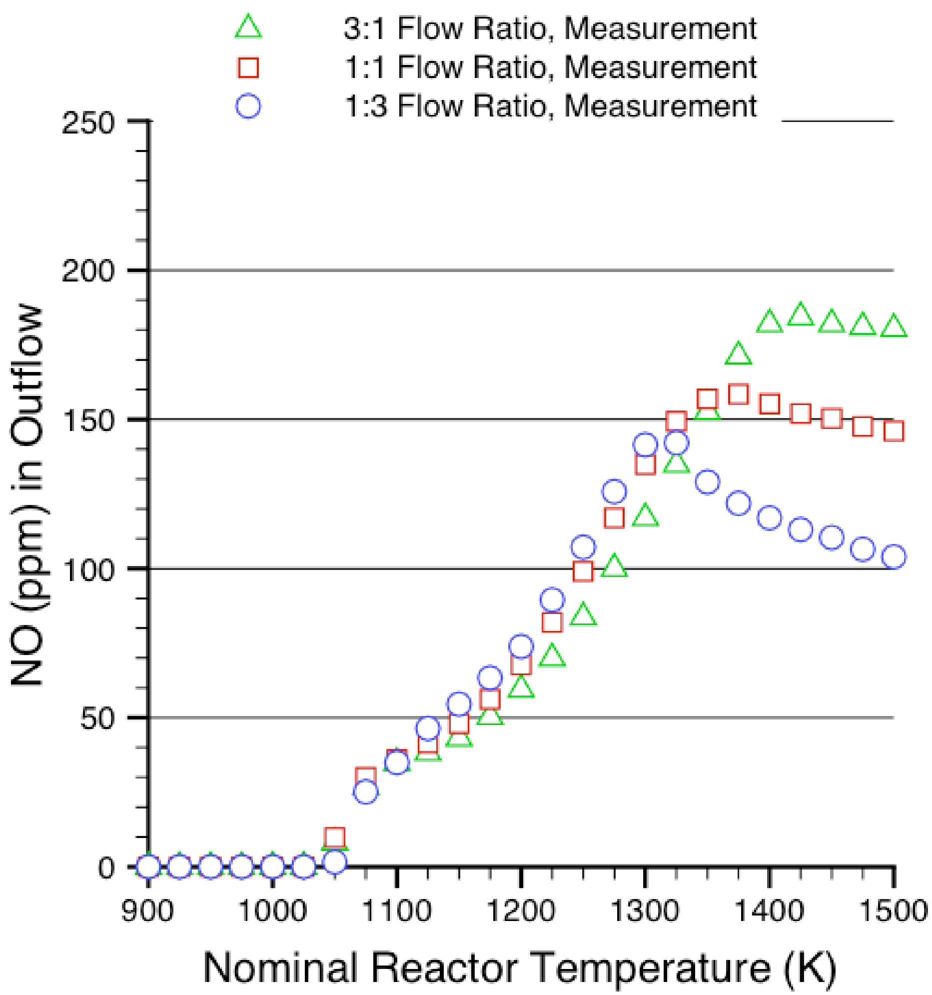
L / m	Fuel	Oxidizer
CH_4	1.0e-3	
NH_3	3.0e-4	
O_2		4.0e-2
H_2O		2.0e-2
N_2	balance	balance

Characterized by:

1. Temperature set point (900-1500 K)
2. Fuel : Oxidizer flow ratio (1 : 3, 1 : 1, 3 : 1)

- Always same total flow (2.0 L / m in standard T & P)
- Always same reactant dosage
- N_2 apportioned to choose the flow ratio

Observations



1. Below 1300 K
   NO independent of flow ratio
   (50 ppm variation)
2. 1300-1400 K
   Qualitative change in behavior
3. Above 1400 K
   NO sensitive to flow ratio

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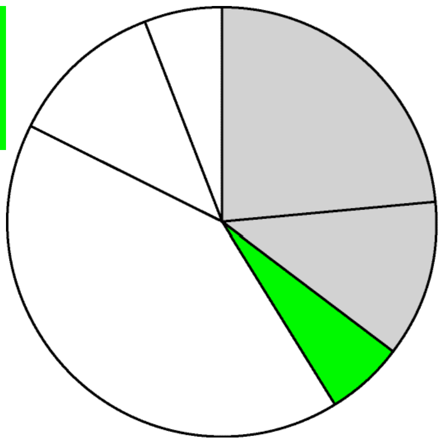
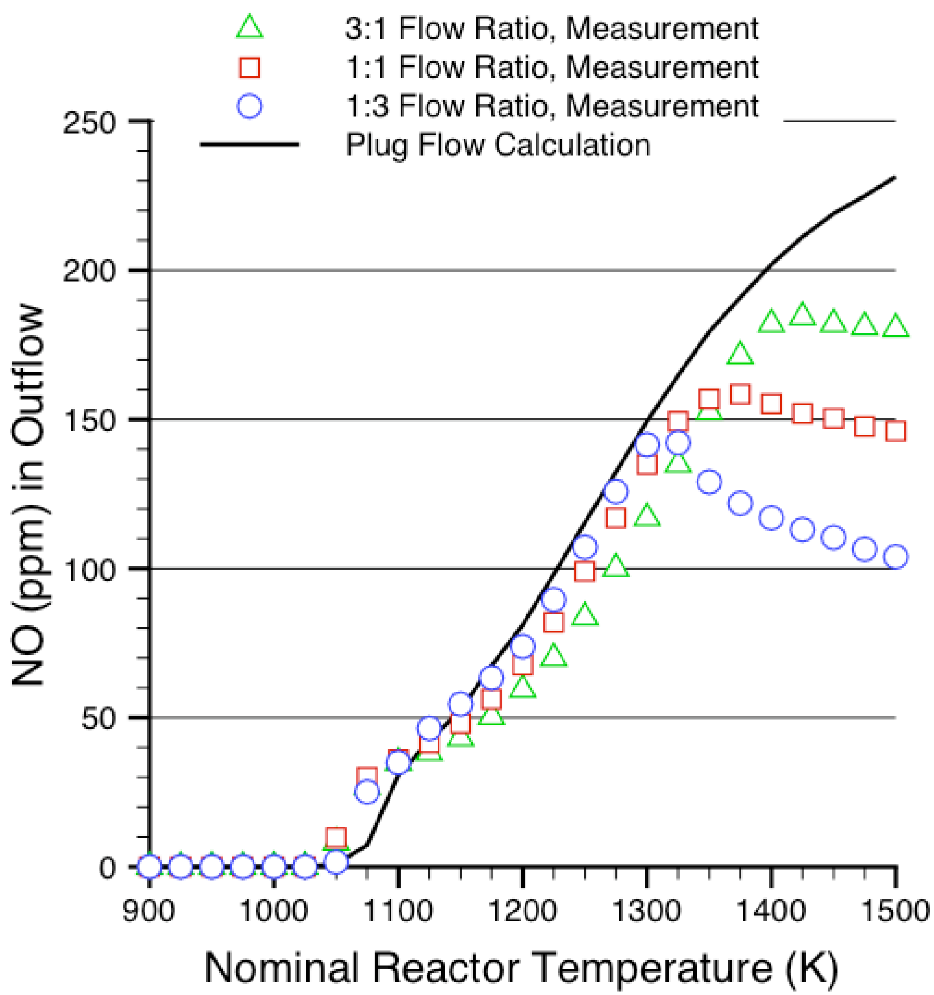


Plug Flow Model



- Mechanism of Glarborg, Alzueta, Dam-Johansen, and Miller, *Combust. Flame* (1998)
- Chemkin's SENKIN by Lutz, et al. (1987)
  - Premixed inflow so no flow ratio dependence (residence time is 1.274 s per 1000 K)
- "Good" agreement with experiment up to 1300 K
  - 60 ppm variation at highest experimental flow ratio

Conclude: reactor has premixed reaction zone below 1300 K.

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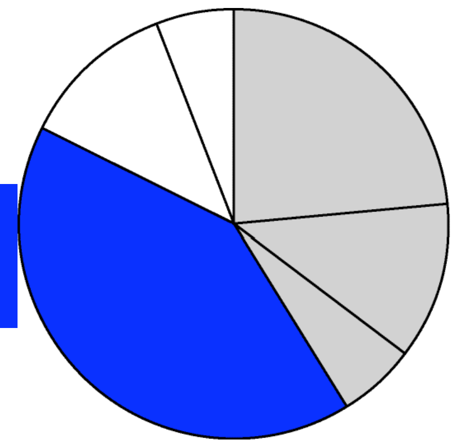
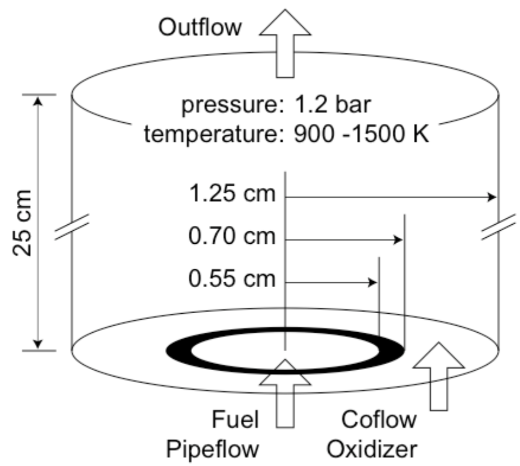


2-D Calculations



NO ppm	1200 K	1300 K	1500 K
1:3 F/O	76	81	85
1:1 F/O			122
3:1 F/O		125	151

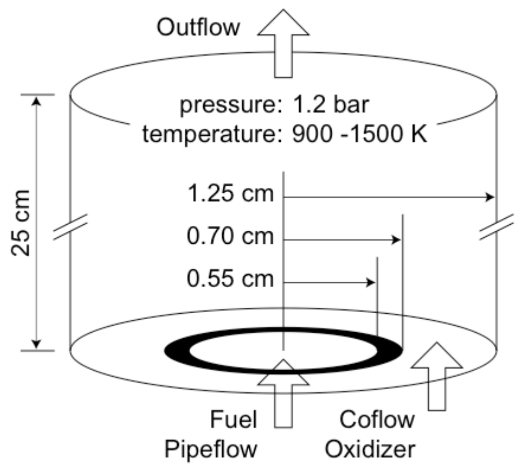
Models:

- 65 species, 447 reaction methane-nitrogen (Glarborg, et al., 1998)
- CHEMKIN kinetics and transport (Kee, et al. 1983, 1986)
- Low Mach number fluid dynamics (Day, Bell, 2000)

Setup:

- R-Z coordinates (1.25 cm radius, 25.0 cm length)
- 193 □ resolution in reaction zone (adaptive mesh)
- Evolve to steady state (1.5 to 2.0 model seconds)

2-D Calculations



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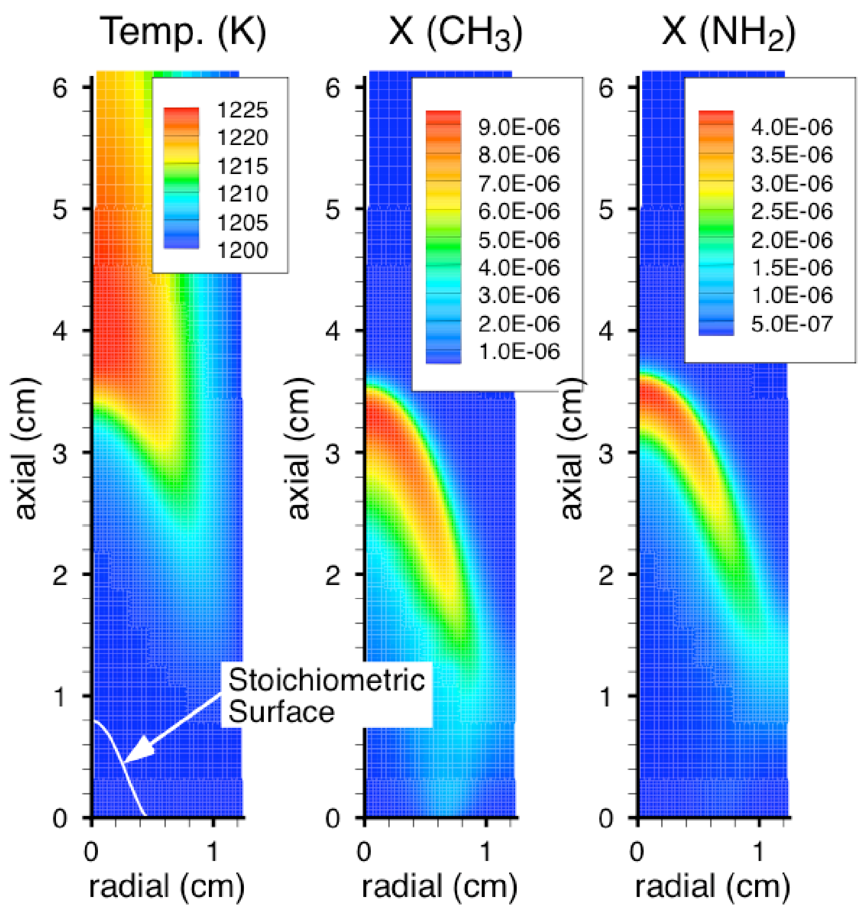
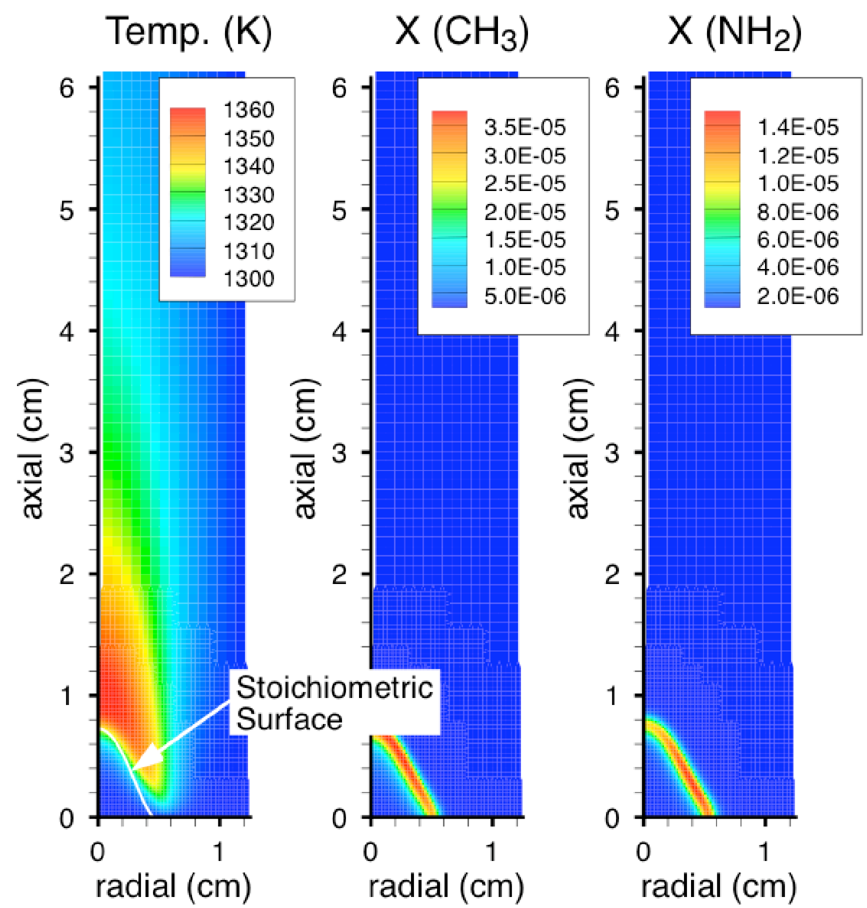
2 Types of Reaction Zones

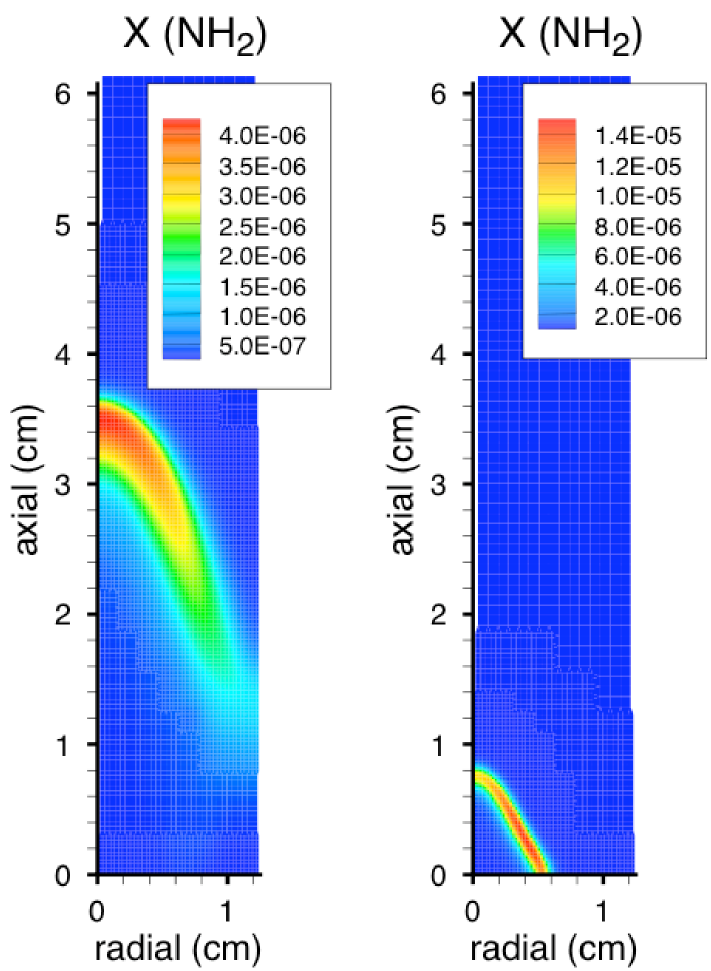
1200 K — 1:3 F/O Flow Ratio — 1300 K





2 Types of Reaction Zones, cont.

1200 K　　1300 K



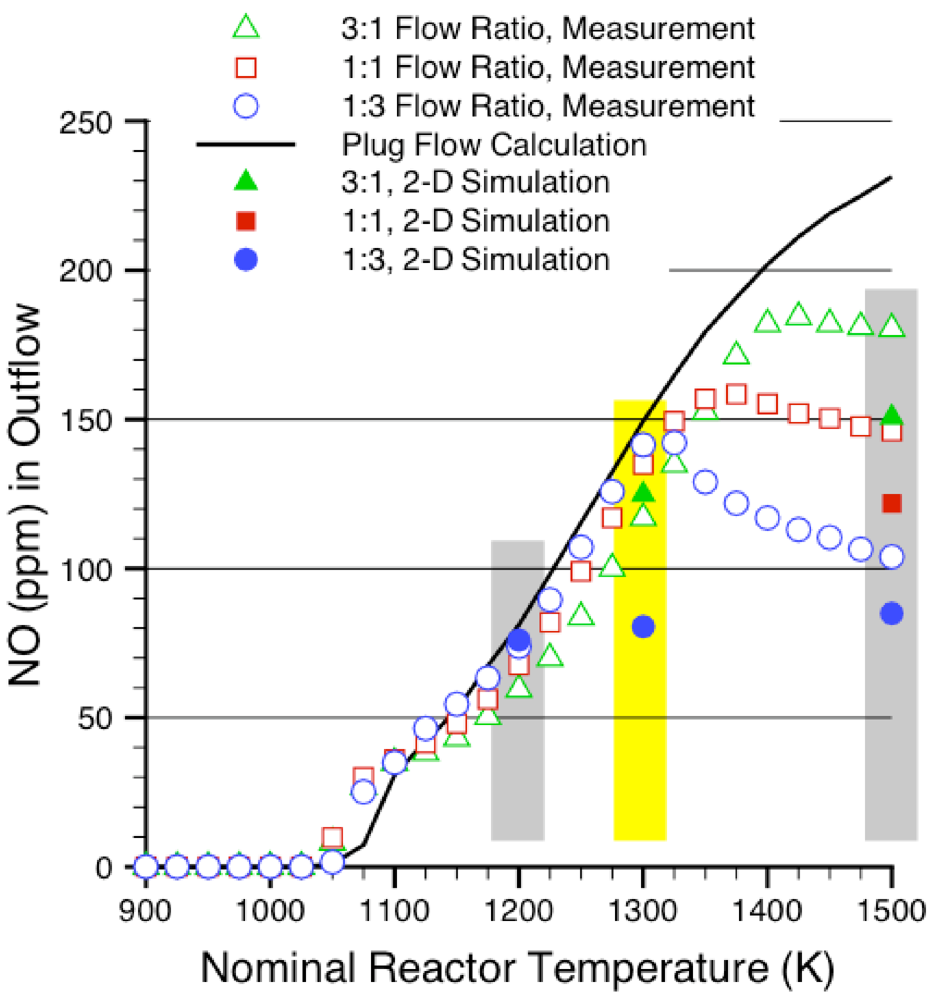
1. Low temperatures
   - Thick, parabolic shape extends across reactor tube
   - Occurs after fuel and oxidizer streams are well mixed (for the 1:3 fuel-oxidizer flow ratio, about 33% of centerline fluid is oxidizer at 3 cm)
   - **Premixed reaction zone**

2. Higher temperatures
   - Thin, cone shape is anchored at lip of inner, fuel tube
   - Occurs at stoichiometric surface

   Non-premixed reaction zone

Note these reaction zones are not self-sustaining flames.

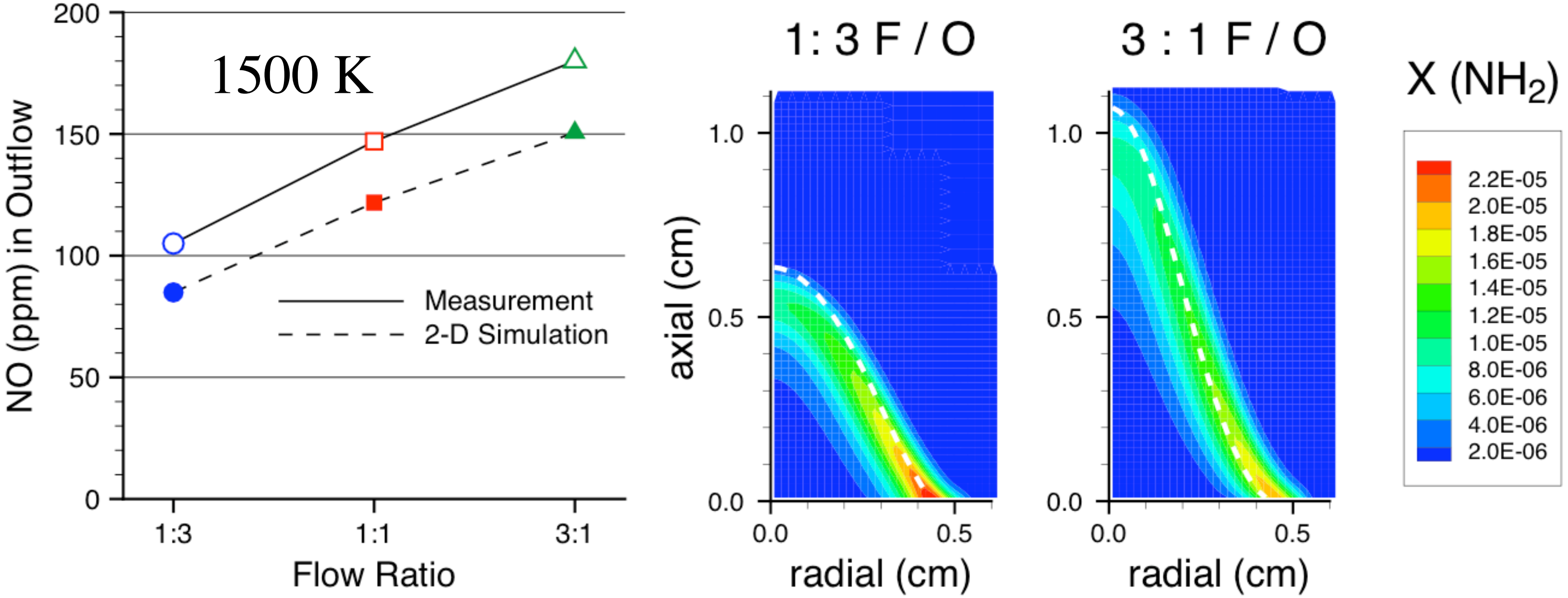
DNS Predictions



- At extremes of the temperature range, the predictions are "good"
  - match at 1200 K
  - within 20% of the experiment at 1500 K
- At bifurcation points, the reactor and the model can be out of synch
  - the NO predictions are bad
  - several possible reasons …

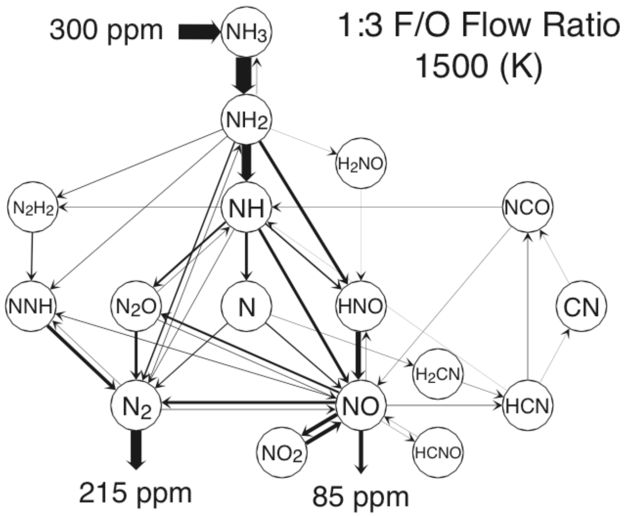
Conclude: reactor has nonpremixed reaction zone above 1400 K.

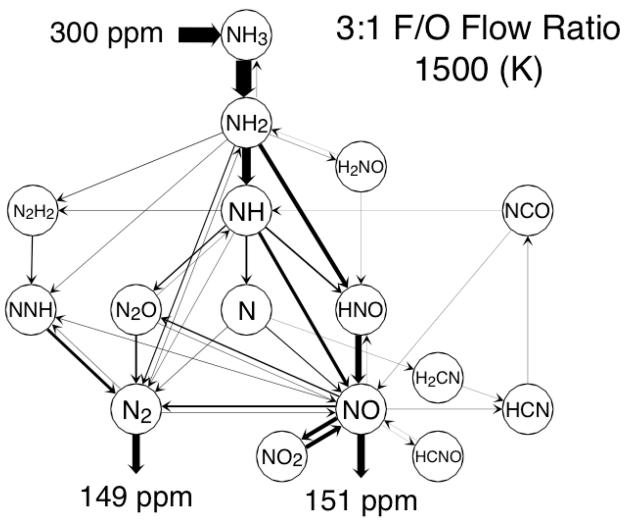
Nonpremixed Reaction Zone



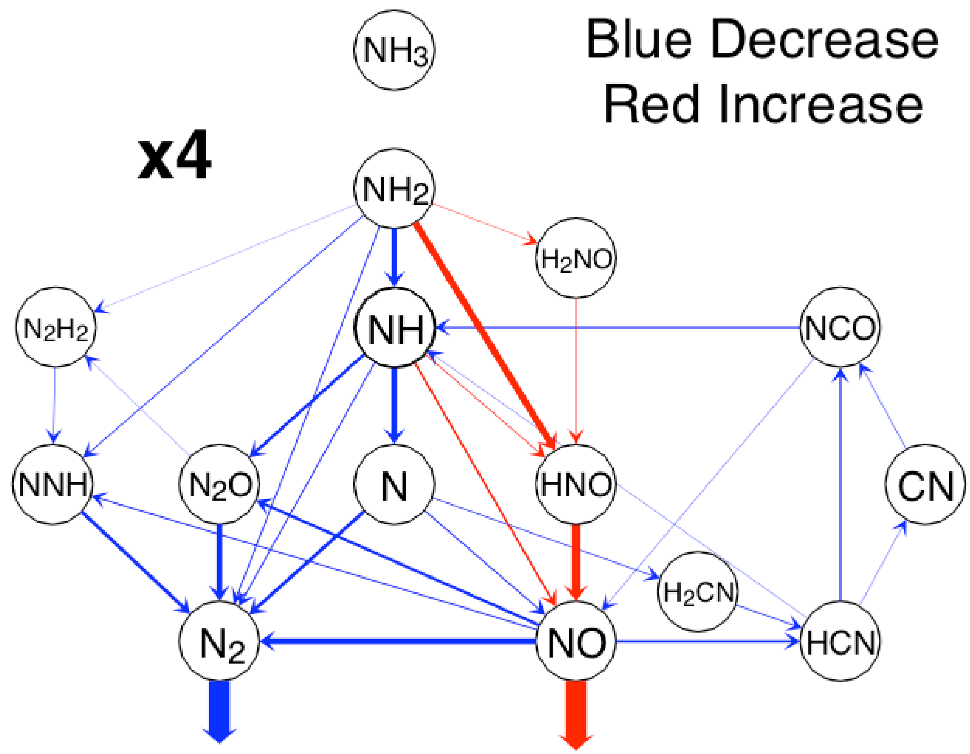
- Predictions are within 20% of measurements when both reactor and model have nonpremixed reaction zones
- At higher fuel : oxidizer flow ratios, the nitrogen chemistry moves toward the lean side of the reaction zone

Shift to Lean-Side Reactions





Subtract Reaction Paths



Most of the change is caused by

$$NH_2 + O \rightarrow HNO + H$$

which is enhanced in the forward direction when NH_2 moves to the lean side of the reaction zone.

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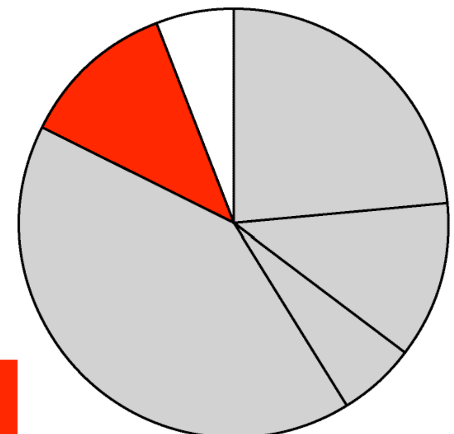


Zwieterung Model

Used to described mixing effects in reactors

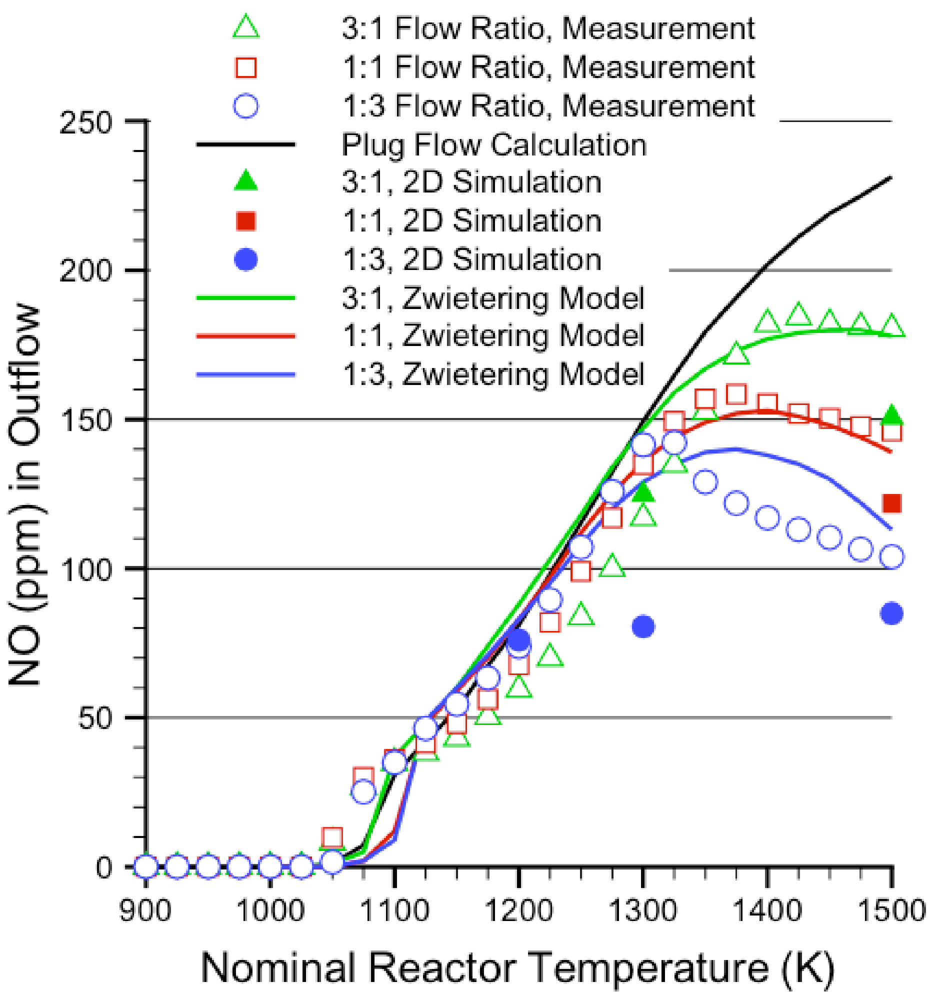
- Assume exponential entrainment of the oxidizer stream into the fuel stream over a mixing time $\square$

$$\frac{d\dot{m}_{fuel}}{dt} = k\dot{m}_{oxid} \qquad k = \frac{\ln(\dot{m}_{oxid,0} / \dot{m}_{oxid,\square})}{\square}$$

- Here, $\square$ is determined from the 2-D simulation as the time to obtain 95% mixing of the two streams on the centerline of the reactor
- Implemented using Chemkin's SENKIN

– Zwieterung, *Chem. Eng. Sci.* (1959)
– Alzueta, et al., *Energy Fuels* (1998)
– Røjel, et al., *Ind. Eng. Chem. Res.* (2000)

Zwieterung Model



- Very good agreement with experiment for the 1:1 and 3:1 F/O flow ratios

Conclude: the mixing model captures surprisingly well the experimental trends.

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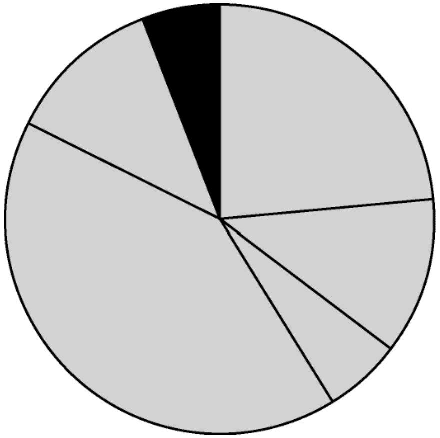

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- Laminar flow reactor bifurcates between stable premixed and stable nonpremixed reaction zones
  - Bifurcations determined by temperature
  - Nonpremixed reaction zone moderates NO production from NH_3
- As in flames, NO production at intermediate temperatures is sensitive to mixing
- Inexpensive 2-D DNS simulations can be used to visualize complex mixing in laminar flow reactors
  - All calculations were done on desktop personal computers
- Entrainment models can be constructed to correctly predict reactor behavior

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Contact author regarding collaborative use of the 2-D DNS software.